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(54) Supported nickel-based catalyst

(57) A supported nickel-based catalyst containing 10-85 % by weight of nickel; of which 40-99 % is in the form of the metal, 0.05-6.7 % by weight of boron, and, optionally, 0.1-10 % by weight of Cu, Ag, Cr, Zr, Th, Sn, Re or one of the group VIII metals. The catalyst is prepared by a method in which nickel dihydroxide and/or nickel hydroxide carbonate, which have been obtained by precipitating a nickel salt with an alkali, are subjected to the action of an alkaline borohydride solution at 20-100°C and pH higher than 10 over a period of 5-60 min. The catalyst mass is then washed, dried, calcined at 300-500°C and finally reduced at 250-480°C to a degree of reduction of 0.40-0.99. The catalyst is useful in the hydrogenation of polyunsaturated organic compounds to the corresponding partly or completely saturated compounds, particularly the hydrogenation of unsaturated fatty acids and their glycerides to the corresponding partly or completely saturated compounds.

SPECIFICATION

Supported nickel-based catalyst

- 5 Supported nickel-based catalyst and use of it in a process of hydrogenation of polyunsaturated organic compounds to the corresponding partly or completely saturated compounds.

- 10 This invention relates to a supported nickel-based catalyst, to a process of preparing the supported nickel-based catalyst, and to the use of such supported nickel-based catalyst in a process of hydrogenating polyunsaturated organic compounds to the corresponding partly or completely saturated compounds.

- 15 Supported nickel catalysts with a carrier such as diatomic earth, alumina or silica gel have long been used as heterogeneous catalysts in the processes of selective hydrogenation or polyunsaturated organic compounds to di- or monosaturated compounds. One of the most important of these processes is the hydrogenation of unsaturated fatty acids bound in vegetable oils and animal fats, or the hydrogenation of free unsaturated fatty acids, to the corresponding partly or completely saturated compounds. At the present time, the annual worldwide volume of oils and fats hydrogenated for further processing to food and technical products exceeds 4.10⁶ ton. This fact and an effort at maximum utilization of all food resources compel the producers to improvements in the hydrogenation technology, where besides on the attainment of optimum economic effect, demand is also made on the selective mode of the process operation.

- 20 Owing to the boiling points of the processed materials, the hydrogenation process is carried out in the liquid phase at an elevated temperature and pressure in the presence of a heterogeneous catalyst, thus representing a comparatively complex three-phase liquid-gas-solid system. Apart from technological parameters of the equipment such as continuous or discontinuous operation, the mode of mass and heat transfer in the system, etc., it is the quality of the catalyst used which is of primary importance. In order to utilize fully the capacity of a hydrogenation unit, it is necessary to attain a high reaction rate, the prerequisite for which is high activity of the catalyst. From the aspect of the possibility of obtaining a product of a required composition, containing preselected esters of fatty acids, emphasis is placed at the same time on selective behaviour of the hydrogenation catalyst. For example, in hydrogenation of vegetable oils such as rape-seed oil or soya bean oil, containing glycerides of linolenic acid, it is required — in view of the enhancement of constancy of the taste and smell of the product — that the glycerides of linolenic acid be substantially or completely removed while the content of glycerides of linoleic acid be reduced as little as possible and the content of glycerides of stearic acid be increased to a minimum extent.

- 25 Nickel catalysts so far used in technical practice do not, as a rule, show high activity along with selectivity for hydrogenation of polyunsaturated organic compounds, and usually only one of the properties

is dominant.

- According to the present invention there is provided a nickel-based catalyst supported on an inorganic carrier such as diatomic earth, alumina or silica gel comprising from 10 to 85 percent by weight of nickel, of which amount 40 to 99 percent is constituted by nickel in the form of the metal, and from 0.05 to 6.7 percent by weight of boron. The catalyst of this invention may further contain from 0.01 to 10 percent by weight of copper, silver, chromium, zirconium, thorium, tin, rhenium, or one of the group VIII metals, or a mixture of at least two of said metals.

- The aforesaid catalyst is prepared in the following way:

- (i) precipitating a suspension of an inorganic carrier in a nickel salt solution with an alkali,
(ii) subjecting the mixture of the inorganic carrier and the precipitated nickel dihydroxide and/or nickel hydroxide carbonate with a composition of $\text{NiCO}_3 \cdot x \text{Ni(OH)}_2 \cdot y \text{H}_2\text{O}$, where x is a number from 1 to 30 including and y is an arbitrary number, to the action of an alkaline borohydride solution in an amount of 0.005 to 1.25 mole borohydride per 1 mole nickel, carrying out this operation at a temperature between 20 and 100°C and at a pH higher than 10 over a period of 5 to 60 min,
(iii) washing and drying the resulting mass,
(iv) calcinating the mass at a temperature between 300 and 500°C, and
(v) reducing the calcinated mass at a temperature between 250 and 480°C to a degree of reduction ranging from 0.40 to 0.99.

- When the supported nickel-based catalyst is also required to contain the aforesaid modifying metals, the mixture of an inorganic carrier and the nickel dihydroxide and/or nickel hydroxide carbonate of the above composition is treated together with an addition of a salt of copper, silver, chromium, zirconium, thorium, tin, rhenium, or one of the group VIII metals, or a mixture of at least two of said salts in an amount corresponding to 0.1 to 10 percent by weight of the metal.

- The present invention further provides a process of hydrogenating polyunsaturated organic compounds to the corresponding partly or completely saturated compounds which comprises contacting hydrogen at a pressure between 1.013×10^5 and 2.7×10^6 Pa with a polyunsaturated organic compound at a temperature between 30 and 240°C in the presence of a supported nickel-based catalyst as hereinbefore set forth. The time of contact is chosen to give the required composition of the product.

- The nickel-based catalyst of this invention is particularly suitable for use as a catalyst of the hydrogenation of unsaturated fatty acids and their glycerides to the corresponding partly or completely saturated compounds. The process is carried out at a hydrogen pressure between 1.013×10^5 and 2.7×10^6 Pa at a temperature between 80 and 240°C. The time of conversion is again chosen to give the required composition of fatty acids in the product. The amount of the catalyst suitably lies within the range from 0.01 to 2 percent by weight of the metallic nickel, based on the weight of the processed

raw material, preferably within the range from 0.02 to 0.06 percent by weight.

The hydrogenation process as herein described may be carried out on both continuous and discontinuous basis.

The exposure of the precipitate obtained by mixing a nickel salt solution with an alkali to an alkaline borohydride solution results in an exchange of a portion of surface hydroxyl groups of the nickel dihydroxide and/or nickel hydroxide carbonate structure with the $(\text{BH}_4)^-$ anion. The finished catalyst then exhibits several times higher activity and selectivity for hydrogenation of polyunsaturated organic compounds to the corresponding partly or completely saturated compounds as compared with a similar product which has not been treated with the alkaline borohydride.

The catalyst of this invention is suitable for use in such processes as hydrogenation of cyclooctadiene to cyclooctene. Far the most important from the industrial point of view is however the hydrogenation of unsaturated fatty acids and their glycerides to the corresponding partly or completely saturated compounds. When the process is conducted on a selective basis, yielding partly hydrogenated vegetable oils, the hydrogenation process is mostly stopped at 0-30 percent by weight of the initial amount of linolenic acid. For example in the processing of rape-seed oil with minimized content of erucic acid, having an initial iodine value of 115, the hydrogenation process is stopped when an iodine value of 90-100 has been reached. Under the given conditions, the content of esters of linoleic acid will be reduced to 50-80 percent by weight of the initial quantity. Thus treated oils are then suitable for further production of various sorts of salad-oil, mayonnaise, margarine, etc.

The selective properties of the catalyst also make it possible to attain a comparatively high yield of oleic acid when hydrogenating vegetable oils. In the processing of rape-seed oil with minimized content of erucic acid, for example, the maximum content of the esters of oleic acid in the product is about 83%, and the obtained product may further be processed for technical purposes.

The catalyst in accordance with this invention is also suitable for hydrogenation of vegetable oils to a product with a melting point of 32-39°C which is further processed to margarine, diabetic fat, etc. It is also useful in the total hydrogenation of vegetable oils or free fatty acids to products with an iodine value of 2-5, where the high activity of the catalyst plays the major role.

The invention will now be illustrated by way of the following examples which are to be understood only as illustrative and not to be taken as limiting it thereto.

Example 1

A suspension of diatomic earth in a nickel nitrate solution at 95°C was added while stirring into a warmed sodium carbonate solution. The precipitation was completed by adding a sodium hydroxide solution in an amount such as to bring the molar alkali-to-nickel ratio to 2:1. The obtained precipitate, which after filtration, washing and drying had the

composition $\text{NiCO}_3 \cdot 10.5 \text{Ni}(\text{OH})_2 \cdot 7 \text{H}_2\text{O}$, was subjected at pH 10.5 to the action of 10% aqueous solution of sodium borohydride (pH = 10) over a period of 60 min. After that, the precipitate was filtered off, washed three times with methanol, calcinated at 350°C, and finally reduced at 360-380°C over a period of 10 h to a degree of reduction of 0.86. The resulting catalyst contained, on the weight basis, 51.1% Ni and 0.8% boron, the remainder being the carrier.

The catalyst prepared in this way exhibited substantially higher activity and selectivity for hydrogenation of cyclooctadiene to cyclooctene in the liquid phase as compared with a catalyst prepared in the same way except that the nickel hydroxide carbonate had not been exposed to sodium borohydride. The quantitative results, including the conditions of the hydrogenation reaction, are summarized in Table I.

Table I

Comparison between the course of hydrogenation of cyclooctadiene to cyclooctene using a catalyst prepared as described in Example 1 (catalyst A) and a similar catalyst prepared without the treatment with sodium borohydride (catalyst B).

Reaction conditions:

temperature 30°C; hydrogen pressure 1.0374×10^5 Pa; catalyst concentration 0.833 g Ni per 1 litre of reaction mixture; solvent n-heptane.

time (min)		CATALYST A			CATALYST B		
		concentration of individual components (mole/litre $\times 10^{-2}$)					
		D	M	S	D	M	S
0	5,44	0	0	5,38	0	0	
5	3,38	1,96	0,04	4,56	0,77	0,05	
10	1,84	3,38	0,11	3,90	1,31	0,18	
20	0,32	4,56	0,50	2,84	1,97	0,55	
30	0,03	4,36	1,02	2,10	2,23	1,01	
40	0	3,88	1,54	1,59	2,28	1,48	
50	0	3,40	2,02	1,18	2,21	1,98	
70	0	2,58	2,86	0,67	1,85	2,84	
90	0	1,92	3,50	0,36	1,44	3,54	
110	0	1,42	4,04	0,21	1,10	4,06	
130	0	1,02	4,44	0,13	0,78	4,48	
150	0	0,72	4,72	0,06	0,56	4,75	

D: cyclooctadiene

M: cyclooctene

S: cyclooctane

Example 2

A nickel nitrate solution containing 10 percent of silver nitrate was treated by the same procedure as described in Example 1. The catalyst obtained on reduction of the sample at 350°C to a degree of reduction of 0.8 contained 45,8 percent by weight of nickel, 0.53 percent by weight of boron, and 0.5 percent by weight of silver, the remainder being the carrier. The catalyst was 3 times more active and 2.8 times more selective for hydrogenation of cyclododecatriene to cyclododecene as compared with the same sample which had not been treated with sodium borohydride.

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Example 3

A precipitation vessel was charged with a suspension of diatomic earth in a nickel chloride solution containing PdCl_2 in an amount corresponding to 0.1% of palladium. After heating to 98°C, the precipitation of nickel hydroxide carbonate was performed by adding sodium carbonate in an amount of 2.1 mole per 1 mole nickel. To the suspension in the mother liquor was then added 0.01 mole % sodium borohydride, and the mixture of pH 13.7 was stirred over a period of 10 min at 98°C. After filtration, washing, drying, and calcinating at 400°C, the catalyst was reduced at 450°C to a degree of reduction of 0.85. The resulting catalyst contained, on the weight basis, 58.2% Ni, 0.85% B, and 0.1% Pd, the remainder being the carrier. The selectivity of the catalyst for the hydrogenation of cyclooctadiene to cyclooctene was enhanced by a factor of 3.1 as a consequence of the treatment with sodium borohydride.

Example 4

A nickel nitrate solution containing diatomic earth was precipitated at 30°C with sodium hydroxide in an amount of 1.5 mole per 1 mole nickel. The obtained suspension of nickel dihydroxide was mixed with a sodium borohydride solution (0.6 mole borohydride per 1 mole nickel), and heated at 70-80°C over a period of 60 min. After filtration, washing, drying, calcination at 300°C and reduction at 350°C to a degree of reduction of 0.63, the result-

tant catalyst contained 28 percent by weight of nickel, and 0.3 percent by weight of boron. The catalyst exhibited 5.3 times higher selectivity for hydrogenation of cyclooctadiene to cyclooctene as compared with a similar sample which had not been treated with the alkaline borohydride.

Example 5

A stainless autoclave equipped with a paddle-wheel agitator was charged with 80 g of refined rape-seed oil with minimized content of erucic acid, and with a catalyst containing 3.8 percent by weight of boron and 27 percent by weight of nickel, 48 percent of the latter being in the form of metallic nickel. The amount of the catalyst was 0.04 percent by weight of nickel, based on the weight of the processed oil. The hydrogenation was carried out at 180°C at a hydrogen pressure of 1.52×10^5 Pa. The changes in the composition of the product during the course of hydrogenation are given in Table II which clearly shows both the high selectivity and high activity of the catalyst. The quality of the obtained products satisfied the requirements for further processing to components of salad oil, mayonnaise, margarine, diabetic fat, etc.

Table II

Hydrogenation of rape-seed oil with minimized content of erucic acid under the conditions specified in Example 5.

time (min)	iodine value	fatty acid content (wt. %)			
		stearic	oleic	linoleic	linolenic
0	115	2,6	59,2	21,3	7,3
3	111	2,8	62,7	19,3	5,7
5	104	2,9	66,7	16,7	4,0
7	98	3,1	70,2	14,8	2,3
9	95	3,3	73,5	12,9	0,9
12	89	3,5	76,8	9,8	0
15	85	3,7	80,7	5,7	0
17	79	5,5	83,0	3,0	0
20	76	9,7	82,0	0	0
24	70	15,2	77,1	0	0
30	63	21,0	71,7	0	0
36	59	26,7	66,2	0	0
45	55	32,2	60,7	0	0

Example 6

Utilizing the same autoclave as described in Example 5, 80 g of sunflower oil of the following composition was hydrogenated:

acid	wt. %	acid	wt. %
palmitic	6.73	arachidic	0.54
palmitoleic	0.14	eicosenoic	0.76
stearic	3.96	behenic	0.81
oleic	20.28	erucic	4.95
linoleic	61.83		

The iodine value, determined by the method of Wijs, was found to be 129. The catalyst from the previous operation was filtered off and recycled in

an amount of 0.03 percent by weight of nickel, based on the weight of the oil. The hydrogenation was carried out at 140°C and a hydrogen pressure of 1.52×10^5 Pa. After 160 min, the melting point of the product reached a value of 33.2°C, and the product had the consistency required for further processing to margarine.

Example 7

80 g of fatty acids with an iodine value of 56 distilled from animal fats was hydrogenated in the same autoclave as described in Example 5. The hydrogenation was carried out at 200°C and a hydrogen pressure of 2.354×10^5 Pa, in the presence of a catalyst containing 0.25 percent by weight of boron and 45 percent by weight of nickel, 87 percent of the latter being in the form of metallic nickel. The amount

of the catalyst was 0.43 percent by weight of nickel, based on the weight of the processed fatty acids. After 90 min an iodine value of 2.5 was reached.

CLAIMS

1. A nickel-based catalyst supported on an inorganic carrier such as diatomic earth, alumina or silica gel, comprising from 10 to 85 percent by weight of nickel, of which 40 to 99 percent is constituted by nickel in the form of the metal, and from 0.05 to 6.7 percent by weight of boron.
2. A nickel-based catalyst as claimed in claim 1 containing from 0.1 to 10 percent by weight of copper, silver, chromium, zirconium, thorium, tin, rhenium or one of the group VIII metals or a mixture of at least two of said metals.
3. A nickel-based catalyst whenever prepared substantially as described in examples 1 to 4.
4. A process for the manufacture of the nickel-based catalyst as claimed in claim 1 which comprises
 - (i) precipitating a suspension of an inorganic carrier in a nickel salt solution with an alkali,
 - (ii) subjecting the mixture of the inorganic carrier and the precipitated nickel dihydroxide and/or nickel hydroxide carbonate with a composition of $\text{NiCO}_3 \cdot x \text{Ni(OH)}_2 \cdot y \text{H}_2\text{O}$, where x is a number from 1 to 30 including, and y is an arbitrary number, to the action of an alkaline borohydride solution in an amount of 0.005 to 1.25 mole borohydride per 1 mole nickel, at a temperature between 20 and 100°C and at a pH higher than 10 over a period of 5 to 60 min,
 - (iii) washing and drying the resulting mass,
 - (iv) calcinating at a temperature between 300 and 500°C,
 - (v) reducing at a temperature between 250 and 480°C to a degree of reduction ranging from 0.40 to 0.99.
5. A process for the manufacture of the nickel-based catalyst as claimed in claim 2 which comprises
 - (i) precipitating a suspension of an inorganic carrier in a nickel salt suspension with an alkali,
 - (ii) subjecting a mixture of the inorganic carrier, the precipitated nickel dihydroxide and/or nickel hydroxide carbonate with a composition of $\text{NiCO}_3 \cdot x \text{Ni(OH)}_2 \cdot y \text{H}_2\text{O}$, where x is a number from 1 to 30 including and y is an arbitrary number, and a salt of copper, silver, chromium, zirconium, thorium, tin, rhenium or one of the group VIII metals or a mixture of at least two of the salts in an amount corresponding to 0.1 to 10 percent by weight of the metal, to the action of an alkaline borohydride solution in an amount of 0.005 to 1.25 mole borohydride per 1 mole nickel, at a temperature between 20 and 100°C and at a pH higher than 10 over a period of 5 to 60 min,
 - (iii) washing and drying the resulting mass,
 - (iv) calcinating at a temperature between 300 and 500°C,
 - (v) reducing at a temperature between 250 and 480°C to a degree of reduction ranging from 0.40 to 0.99.
6. A process for the manufacture of a nickel-based catalyst substantially as herein described.
7. A nickel-based catalyst when made by the pro-

cess of any of claims 4 and 5.

8. A process of hydrogenation of polyunsaturated organic compounds to the corresponding partly or completely saturated compounds in the liquid phase which comprises contacting hydrogen at a pressure of 1.013×10^5 to 2.7×10^6 Pa with a polyunsaturated organic compound at a temperature between 30 and 240°C in the presence of a nickel-based catalyst as claimed in any of claims 1 to 3 or in claim 7 for a time such as to give a required composition of the product.
9. A process of hydrogenation of unsaturated fatty acids and/or their glycerides to the corresponding partly or completely saturated compounds in the liquid phase which comprises contacting hydrogen at a pressure of 1.013×10^5 to 2.7×10^6 Pa with an unsaturated fatty acid or a mixture of unsaturated fatty acids and/or their glycerides at a temperature between 80 and 240°C in the presence of a nickel-based catalyst as claimed in any of claims 1 to 3 or in claim 7 for a time such as to give a required composition of the product.
10. A process as claimed in claim 9 in which the amount of the catalyst is between 0.01 and 2 percent by weight of metallic nickel, based on the weight of the processed raw material.
11. A process as claimed in claim 10 in which the amount of the catalyst is between 0.02 and 0.06 percent by weight of the metallic nickel, based on the weight of the processed raw material.
12. Partly or completely saturated organic compounds whenever prepared substantially as described herein using the nickel-based catalyst as claimed in any of claims 1 to 3 or in claim 7.

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